$[Co_{11}Te_7(CO)_{10}]^{2-}$, a Novel Cobalt Telluride Cluster Anion containing a Body-centred Pentagonal-prismatic Cobalt Framework, and $[Co_4Te_2(CO)_{11}]$, a Possible Precursor with a Metal-deficient Pentagonal-planar Cobalt Frame

Renate Seidel, Rainer Kliss, Stefan Weissgräber and Gerald Henkel*

Gerhard-Mercator-Universität Duisburg, Lotharstrasse 1, Fachgebiet Anorganische Chemie/Festkörperchemie, D-47048 Duisburg, Germany

$[Co_{11}Te_7(CO)_{10}]^{2-}$, an unprecedented undecanuclear cluster anion consisting of a body-centred pentagonal-prismatic cobalt framework completely capped by two μ_6 and five μ_4 telluride ions, and $[Co_4Te_2(CO)_{11}]$, a possible tetranuclear precursor, are described.

Compounds with unique structural features and unusual reactivities are often observed when sulfur-, selenium- or tellurium-containing ligands are incorporated into transition metal clusters.[1] In particular, the selenium- and tellurium-containing complexes are currently receiving considerable attention,[2] because their chemistry is substantially different from that of the sulfides[3] and also because they are finding uses as convenient precursors to solid materials.[4]

In an approach to synthesize homonuclear complexes with unprecedented metal frameworks, we investigated the reaction system $[Co_2(CO)_8]$, Na_2Te_2 and $[Ph_4P]Cl$ in methanol under solvothermal conditions. In the case of a 3 : 2 : 3 molar ratio of the components (80 °C, 64 h), we were able to isolate deep black crystals of **1** containing the undecanuclear cluster anion **2**. At a molar ratio of 4 : 2 : 1, black–violet needles of the tetranuclear cluster complex **3** were isolated instead.† The structures of **1** and **3** were determined by X-ray crystallography.‡

$[Ph_4P]_2[Co_{11}Te_7(CO)_{10}]$ **1**

$[Co_{11}Te_7(CO)_{10}]^{2-}$ **2**

$[Co_4Te_2(CO)_{11}]$ **3**

Crystals of **1** are composed of discrete anions **2** of idealized D_{5h} symmetry and $[Ph_4P]^+$ cations in a ratio of 1 : 2. The structure of **2** is shown in Figs. 1 and 2. The anion contains the novel Co_{11} cluster core, which is a slightly elongated pentagonal-prismatic array of cobalt atoms with a single cobalt atom residing in the centre of the prism (Fig. 2). The only other metal cluster with a related pentagonal-prismatic geometry is the Pt_{19} core of $[Pt_{19}(CO)_{22}]^{4-}$.[5] The symmetry distortion can be attributed to the encapsulated Co atom which is 2.558 Å away from its Co neighbours. As a result, the average Co–Co distance within the pentagonal-planar faces (2.583 Å) is *ca.* 0.04 Å shorter than the corresponding distance between atoms of adjacent metal pentagons (2.622 Å). These distances are in the range of normal Co–Co bonds observed, *e.g.* in the tetranuclear complex $[Co_4Te_2(CO)_{10}]$ (2.58 Å).[6]

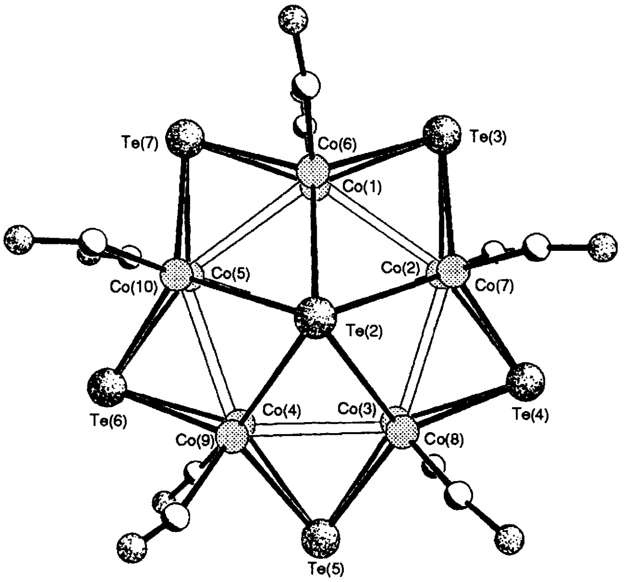

Fig. 1 $[Co_{11}Te_7(CO)_{10}]^{2-}$: Projection with atomic labels showing the overall fivefold symmetry [Co(11) and Te(1) are hidden by Te(2)]. Characteristic distances [Å] and angles [°]: Co(1)–Co(2) 2.567(4), Co(1)–Co(6) 2.622(3), Co(1)–Co(11) 2.534(3), Co(1)–Te(1) 2.562(2), Co(1)–Te(3) 2.516(3), Co(11)–Te(1) 2.642(2), Co(1)–C(1) 1.76(1), Co(1)–Te(1)–Co(2) 59.8(1), Co(1)–Te(1)–Co(3) 108.5(1), Co(1)–Te(1)–Co(11) 58.3(1), Co(1)–Te(3)–Co(2) 61.3(1), Co(1)–Te(3)–Co(7) 93.7(1).

Each of the five Co_4 squares is capped by a μ_4-Te ligand with a mean Co–Te bond distance of 2.510 Å. In addition, two μ_6-Te ligands are situated above the centres of the pentagonal Co faces, forming Co–Te bonds of 2.569 Å length. These ligands are also bound to the encapsulated Co atom at distances of 2.642(2) and 2.647(2) Å, respectively. According to our knowledge, this unusual bridging mode of a chalcogenide ion has been observed for the first time resulting in a linear Te–Co–Te coordination. The other Co atoms are in a tetrahedral ligand environment due to ten terminally-bonded CO groups. They are surrounded by one CO and three Te ligands each.

The encapsulated Co atom is the common vertex of a total of five nearly regular octahedral $CoCo_4Te$ units which are connected *via* common faces to form the complete $Co_{10}Co(\mu_6\text{-}Te)_2(\mu_4\text{-}Te)_5$ framework observed in **2**. The mean oxidation state of Co is calculated to be +1.09. This value is in agreement with a mixed-valent state in which the encapsulated metal atom is formally divalent and the remaining ones are monovalent.

The cluster complex **3** with idealized C_{2v} symmetry shows some striking structural similarities with characteristic core

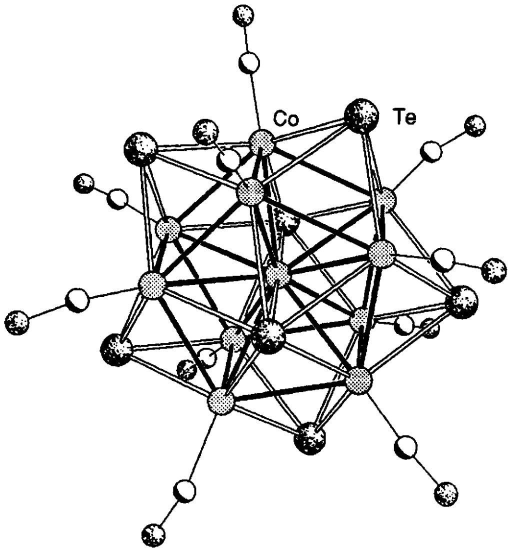

Fig. 2 $[Co_{11}Te_7(CO)_{10}]^{2-}$: Perspective view with outline of the body-centred pentagonal-prismatic cobalt framework (solid bonds) and bridging telluride ions (open bonds)

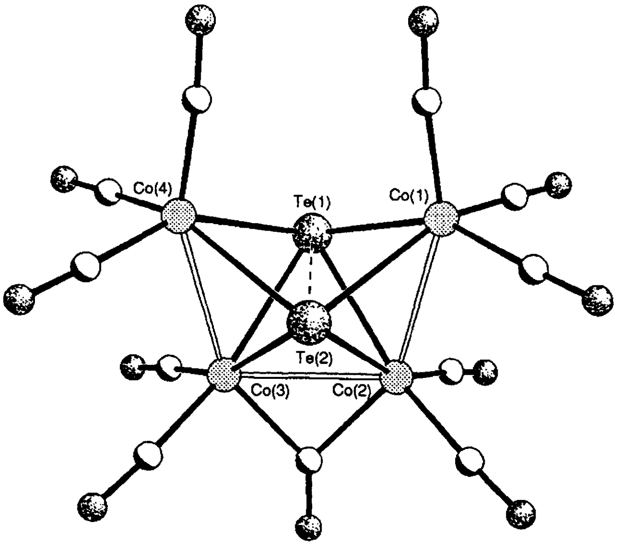

Fig. 3 $[Co_4Te_2(CO)_{11}]$: Molecular structure and atomic labels. Characteristic distances [Å] and angles [°]: Co(1)–Co(2) 2.630(2), Co(2)–Co(3) 2.592(2), Co(3)–Co(4) 2.626(2), Co(1)···Co(4) 3.795(2), Co(1)–Te(1) 2.601(2), Co(1)–Te(2) 2.598(2), Co(2)–Te(1) 2.593(2), Co(2)–Te(2) 2.591(2), Co(3)–Te(1) 2.589(2), Co(3)–Te(2) 2.587(2), Co(4)–Te(1) 2.609(2), Co(4)–Te(2) 2.618(2), Te(1)···Te(2) 3.063(1); Co(1)–Te(1)–Co(2) 60.8(1), Co(1)–Te(1)–Co(3) 103.7(1), Co(1)–Te(1)–Co(4) 93.5(1), Co(2)–Te(1)–Co(3) 60.0(1), Co(2)–Te(1)–Co(4) 104.1(1), Co(3)–Te(1)–Co(4) 60.7(1), Te(1)–Co(1)–Te(2) 72.2(1), Te(1)–Co(2)–Te(2) 72.4(1), Te(1)–Co(3)–Te(2) 72.6(1), Te(1)–Co(4)–Te(2) 71.7(1).

portions of the cluster anion **2** (Fig. 3). Its tetranuclear metal frame is a chain of cobalt atoms which are connected by metal–metal bonds. This chain fits well into the regular pentagonal subunit of **2** by small adjustments of the terminal atoms leaving one metal site empty. Similar metal frameworks have also been observed in structurally related Sb and Bi complexes.[7] The trapezoidal cobalt arrangement is in accordance with the 18-electron rule which predicts three Co–Co single bonds for the total of 66 valence electrons observed here. These bonds are 2.630(2) [Co(1)–Co(2)], 2.592(2) [Co(2)–Co(3)] and 2.626(2) Å [Co(3)–Co(4)] in length. Other tetranuclear carbonyl complexes with chalcogen ligands of formula $[M_2M'_2X_2(CO)_{11}]$ (*e.g.* M, M′ = Fe, X = S;[8] M, M′ = Ru, X = Te;[9] M, M′ = Ru, X = Se;[10] M = Ru, M′ = Fe, X = Te;[11] M = Co, M′ = Fe, X = S)[12] have four metal–metal bonds due to a total of 62 (M = Fe or Ru) or 64 (M = Co) valence electrons, respectively. In contrast, the distance of 3.795(2) Å between Co(1) and Co(4) is much longer in accordance with the predicted non-bonding interaction. This distance is on average 0.11 Å longer than the shortest non-bonding Co···Co interactions observed in **2**. The four Co atoms are bridged by two μ_4-Te ligands with an average Co–Te bond length of 2.598 Å [2.606 Å for Co(1) and Co(4), 2.590 Å for Co(2) and Co(3), respectively]. Due to the long non-bonding Co(1)···Co(4) separation, the telluride ions have to approach each other at a distance of 3.063(1) Å. The coordination of the four formally monovalent cobalt atoms is completed by ten terminally-bonded CO groups and one symmetric CO bridge resulting in square-pyramidal ligand arrangements.

The results of our investigation clearly demonstrate that the chemistry of transition metals with telluride ligands is much more versatile than might be expected from the chemical behaviour presently known.

Financial support from the Deutsche Forschungsgemeinschaft (DFG), from the Bundesminister für Forschung und Technologie (BMFT) and from the Fonds der Chemischen Industrie is gratefully acknowledged.

Received, 5th September 1994; Com. 4/05421K

Footnotes

† A compound of the same composition has been mentioned in the literature[13] but no details concerning synthesis and structure have been published so far: L. F. Bogan, Jr., T. B. Rauchfuss and A. L. Rheingold, *J. Am. Chem. Soc.*, 1985, **107**, 3843.

‡ *Crystal data*: Siemens P4RA four circle diffractometer, rotating anode generator, Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator, scintillation counter, T = 150 K, empirical absorption corrections; direct methods, full-matrix least-squares refinements, non-hydrogen atoms anisotropic, H atoms at idealized positions, one common isotropic temperature factor for H within each residue, one extinction parameter, one scaling factor.

1: $C_{58}H_{40}Co_{11}O_{10}P_2Te_7$, M = 2500.27, triclinic, a = 14.457(8), b = 14.470(7), c = 19.244(11) Å, α = 79.15(4), β = 70.05(4), γ = 62.19(3)°, V = 3344.88 Å^3, space group $P\bar{1}$, Z = 2, D_x = 2.482 g cm^{-3}, μ(Mo-Kα) = 5.74 mm^{-1}, transmission range 0.984–0.473, $2\theta_{max}$ = 48°, ω-scan, crystal dimensions *ca.* 0.47 × 0.28 × 0.18 mm, 10493 unique reflections, R (R_w) = 0.0565 (0.0614) for 8126 reflections with $I > 2\sigma(I)$, 795 variables.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

3: $C_{11}O_{11}Co_4Te_2$, M = 799.03, monoclinic, a = 9.544(2), b = 6.984(2), c = 28.061(6) Å, β = 92.01(1)°, V = 1869.26 Å^3, space group $P2_1/n$, Z = 4, D_x = 2.839 g cm^{-3}, μ(Mo-Kα) = 6.60 mm^{-1}, transmission range 0.983–0.644, $2\theta_{max}$ = 54°, ω-scan, crystal dimensions *ca.* 0.65 × 0.23 × 0.17 mm, 2943 unique reflections, R (R_w) = 0.0365 (0.0348) for 2092 reflections with $I > 2\sigma(I)$, 254 variables.

References

1 I. G. Dance and K. Fisher, *Prog. Inorg. Chem.*, 1994, **41**, 637; L. C. Roof and J. W. Kolis, *Chem. Rev.*, 1993, **93**, 1037; B. Krebs and G. Henkel, *Angew. Chem.*, 1991, **103**, 785; *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 769; D. Fenske, J. Ohmer, J. Hachgenei and K. Merzweiler, *Angew. Chem.*, 1988, **100**, 1300; *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1300.

2 M. A. Ansari and J. A. Ibers, *Coord. Chem. Rev.*, 1990, **100**, 223; M. G. Kanatzidis and S.-P. Huang, *Coord. Chem. Rev.*, 1994, **130**, 509.

3 J. W. Kolis, *Coord. Chem. Rev.*, 1990, **105**, 195.

4 J. G. Brennan, T. Siegrist, S. M. Stuczynski and M. L. Steigerwald, *J. Am. Chem. Soc.*, 1989, **111**, 9240; R. C. Haushalter, C. M. O'Connor, J. P. Haushalter, A. M. Umarji and G. K. Shenoy, *Angew. Chem.*, 1984, **96**, 147; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 169.

5 D. M. Washecheck, E. J. Wucherer, L. F. Dahl, A. Ceriotti, G. Longoni, M. Manassero, M. Sansoni and P. Chini, *J. Am. Chem. Soc.*, 1979, **101**, 6110.

6 R. C. Ryan and L. F. Dahl, *J. Am. Chem. Soc.*, 1975, **97**, 6904.

7 T. A. Albright, K. A. Yee, J.-Y. Saillard, S. Kahlal, J.-F. Halet, J. S. Leigh and K. H. Whitmire, *Inorg. Chem.*, 1991, **30**, 1179.

8 R. D. Adams, J. E. Babin, J. Estrada, J.-G. Wang, M. B. Hall and A. A. Low, *Polyhedron*, 1989, **8**, 1885.

9 P. Mathur, B. H. S. Thimmappa and A. L. Rheingold, *Inorg. Chem.*, 1990, **29**, 4658.

10 B. F. G. Johnson, T. M. Layer, J. Lewis, A. Martin and P. R. Raithby, *J. Organomet. Chem.*, 1992, **429**, C41.

11 P. Mathur, I. J. Mavunkal, V. Rugmini and M. F. Mahon, *Inorg. Chem.*, 1990, **29**, 4838.

12 H. Vahrenkamp and E. J. Wucherer, *Angew. Chem.*, 1981, **93**, 715; *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 680.

13 C. E. Strouse, Ph.D. Thesis, University of Wisconsin, Madison, 1969.